

THE SIZE-DEPENDENT ALLOYING EFFECT OF METALLIC NANOPARTICLES AT ROOM TEMPERATURE

Understanding the structure of nanoparticles is the first step in understanding their unusual physical properties. With this focus, we have determined the local structure around atoms in the nanoparticles of Au and Au/Ag clusters using x-ray absorption spectroscopy at the Advanced Photon Source. The results on the population of shells around either Au or Ag atoms in Au/Ag clusters are inconsistent with conventional diffusion models. For example, when Ag is deposited on the large (20-nm) nanoparticles, small numbers of Ag atoms are found around Au atoms. On the other hand, when Ag is deposited on the small (2.5-nm) nanoparticles, Au atoms coordinate with a larger fraction of Ag and close to the random alloy.

Nanometer-size particles (nanoparticles) have generated tremendous excitement in the last few years, both for fundamental science and for technological applications such as catalysis and optoelectronics. There have even been artistic applications. For example, gold (Au) nanoparticles are known to show red color rather than a familiar metallic yellow for a bulk Au, and therefore have been used as a ruby-red pigment for stained glass since the 17th century. Optical properties such as ultraviolet light absorption by a surface plasmon excitation have been studied extensively, but few detailed structural studies have been performed, primarily due to the limitation of the experimental techniques. When the size becomes small to nanometers and the large fraction of the atoms is near the surface [1], the structure and stability of the particle would be expected to differ from three-dimensional bulk crystals.

Of course, nanoparticles of a single metallic species are still interesting, but in our present study, we focus on the binary core-shell nanoparticles, especially their interface structure (e.g., the degree of interdiffusion and alloy formation). This is itself an interesting topic from a fundamental viewpoint and is important for application to bimetallic catalysis [2].

As for studying real-space images, an electron microscope would be one of the most appropriate

methods. Indeed, we can get some ideas about structures, but the information is not quantitative. In addition, diffraction techniques have limitations for accessing the interface. Each particle consists of ~2,000 atoms, which corresponds to only several layers of atoms without long-range order.

In our study, we employed x-ray absorption fine structure (XAFS) using x-rays at the MR-CAT undulator beamline at the Advanced Photon Source [3]. XAFS is an oscillation in the x-ray absorption coefficient as a function of incident x-ray energy just above the absorption edge [4]. This oscillation is due to the interference of outgoing photoelectron waves and backscattered from the surrounding atoms near an x-ray-excited atom. Detailed analysis provides local structural information around the chosen elements, including interatomic distances, the distribution of these distances, and the numbers and often the atomic species of surrounding atoms within ~10 Å. XAFS is particularly suitable to the study of the interface of nanoparticles due to their large fraction of the interface atoms in the particles. The present studies involve the Au nanoparticles with a deposited silver (Ag) shell (hereafter Au/Ag). Au/Ag nanoparticles have very similar atomic size and are completely miscible as a bulk phase at any composition. Since we can distinguish the scattering from either Au or Ag due to the large difference of the XAFS

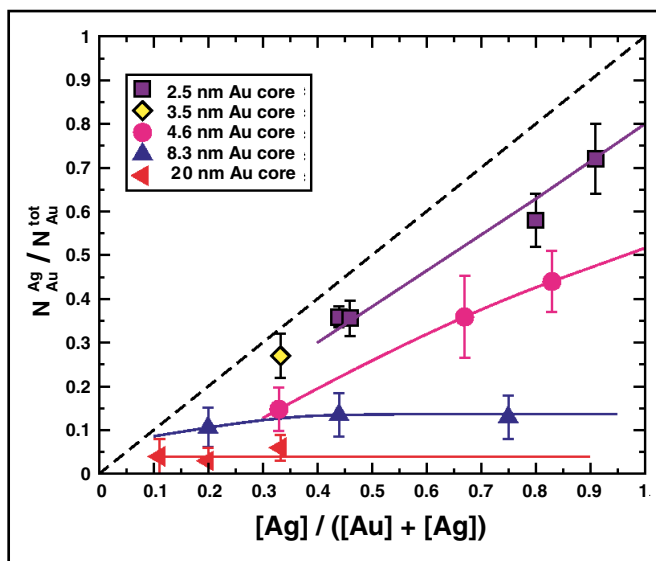


FIG. 1. The relative number of Ag atoms surrounding Au as a function of the Ag concentration $[Ag]/([Au] + [Ag])$ for nanoparticles of various Au core radii and Ag shell thicknesses. The dashed line corresponds to a random alloy; with a distinct interface, the number of Ag atoms about Au should be small. We see clearly the size-dependent alloying effects: When the Au core size is as large as 20 nm, it has a small value, indicating the distinct interface, which does not change much with further deposition, indicating the deposited Ag just stacks on the core. On the other hand, when Ag is deposited on 2.5-nm Au core, it is close to random alloy formation. Note that further deposition of Ag does not inhibit mixing Au and Ag, suggesting that surface melting does not explain the alloying.

scattering function with the photoelectron wave number, XAFS has an advantage over diffraction methods for atomic combinations with a small difference of lattice constants.

Pure Au and Au/Ag nanoparticles with various thicknesses of Ag deposited on various sizes of Au core (from 2.5 to 20 nm in diameter) were synthesized by a radiolysis-initiated reduction method, which provides a narrow size distribution of the particles. Since we are particularly interested in their natural properties, it is emphasized that we measured particles in *aqueous solutions* (i.e., *without any solid support*), which was often used in most previous structural studies. This point is important because the shape of the nanoparticles might be affected by the contact with the solid, especially when the size becomes small. For this reason, the typical metal concentration is as low as 5×10^{-4} M to

avoid coagulating the particles. During and immediately after deposition, the core-shell structure was verified by optical methods; therefore, our main interest is how the structures of nanoparticles initially having distinct core-shell structures change as a function of size. Between synthesis and the time the samples were measured with XAFS, the samples were kept at room temperature to avoid possible temperature effects on alloying.

How can we see the interface by XAFS? As mentioned, we can identify Au/Ag atoms around Au or Ag atoms and obtain their coordination numbers. If no mixing or small mixing of Au and Ag atoms occurred at the interface, Au atoms will coordinate with few Ag atoms but mostly with Au atoms. On the other hand, if a large amount of mixing occurs, Au atoms will coordinate with a large fraction of Ag atoms. Figure 1 shows our XAFS results. The fraction of Ag atoms at the first neighbor of Au atoms is plotted as a function of the fraction of Ag in each nanoparticle. We can see clearly a size-dependent alloying effect from this graph. When Ag is deposited on the large (20-nm) nanoparticles (Fig. 2a), small numbers of Ag atoms are found around Au atoms and do not change much with the further deposition of Ag, indicating a *distinct interface and the further deposition of Ag just stacks on the surface*. On the other hand, when Ag is deposited on the small (2.5-nm) nanoparticles (Fig. 2b), Au atoms coordinate with a larger fraction of Ag and *close to the random alloy*. Furthermore, the value increases with

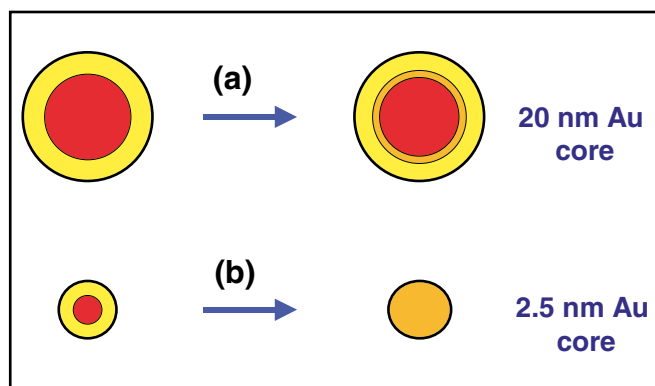


FIG. 2. A schematic of the size-dependent alloying effect: Au (red), Ag (yellow), and mixing region (orange). (a) For 20-nm Au core nanoparticles, the mixing is limited around the interface, whereas (b) for 2.5-nm Au core nanoparticles, nearly random alloy formation is realized.

the farther deposition, indicating that the additionally deposited Ag contributes to the mixing of Au/Ag atoms. The penetration of Ag atoms for the 2.5-nm nanoparticles corresponds to ~ 10 Å from the initial interface.

These experimental results are inconsistent with simple bulk diffusion. The bulk diffusion coefficient in miscible Au/Ag alloy is very small – of the order $\sim 10^{-16}$ Å²/s at room temperature. To be consistent with our data, a ripening time of $\sim 10^{-9}$ years at room temperature would be required; the measurements were actually performed several days after the synthesis of the nanoparticles. Bulk diffusion is also incapable of explaining the observed size dependence of diffusion in a simple way. Furthermore, because the mixing of atoms proceeds by a further deposition of Ag on the 2.5-nm Au nanoparticles, the enhanced diffusion cannot be explained by surface melting. Other mechanisms are being considered for the smaller nanoparticles, with measurements of temperature dependence and studies involving other metals being compared to theoretical calculations and molecular dynamic simulations.

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REFERENCES

- [1] About half of the atoms are facing the surface for 2.5-nm nanoparticles.
- [2] For example, many studies can be found in *Catalysis Today* and *Journal of Catalysis*.
- [3] C.U. Segre, N.E. Leyarovska, L.D. Chapman, W.M. Lavender, P.W. Plag, A.S. King, A.J. Kropf, B.A. Bunker, K.M. Kemner, P. Dutta, R.S. Duran, and J. Kaduk, CP521, *Synchrotron Radiation Instrumentation: Eleventh U.S. National Conference*, P. Pianetta et al., eds., 419-422 (Amer. Inst. Phys., NY, 2000).
- [4] See, for example, *X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES*, edited by D.C. Koningsberger and R. Prins (Wiley, NY, 1988).

T. Shibata,¹ B. Bunker,¹ A. Henglein,² Z. Zhang,² D. Meisel,² S. K. Cheong,¹ M. Boyanov¹

¹ Department of Physics, University of Notre Dame, South Bend, IN, U.S.A.

² Department of Chemistry and Biochemistry and Radiation Laboratory, University of Notre Dame, South Bend, IN, U.S.A.